Supplementary Information (SI)

Unveiling different physicochemical properties of M-doped β-$NaFeO_2$ (where M = Ni or Cu) materials evaluated as CO_2 sorbents: A combined experimental and theoretical analysis

Nayeli Gómez-Garduño[a], Daniel G. Araiza[a,b,*], Christian A. Celaya[c,d,*], Jesús Muñiz[c], Heriberto Pfeiffer[a]

[a]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, Del. Coyoacán, C.P. 04510, Ciudad de México, Mexico

[b]Present address: Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, Ciudad de México, C.P. 04510, Mexico

[c]Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Priv. Xochicalco s/n, Col. Centro, Temixco, C.P. 62580, Morelos, Mexico

[d] Present address: Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Km 107 Carretera Tijuana-Ensenada, Ensenada, B.C., C.P. 22800, Mexico.

*Corresponding author: araiza@materiales.unam.mx (D.G. Araiza) and acelaya@ier.unam.mx (C.A. Celaya)

S.1 Characterization of materials

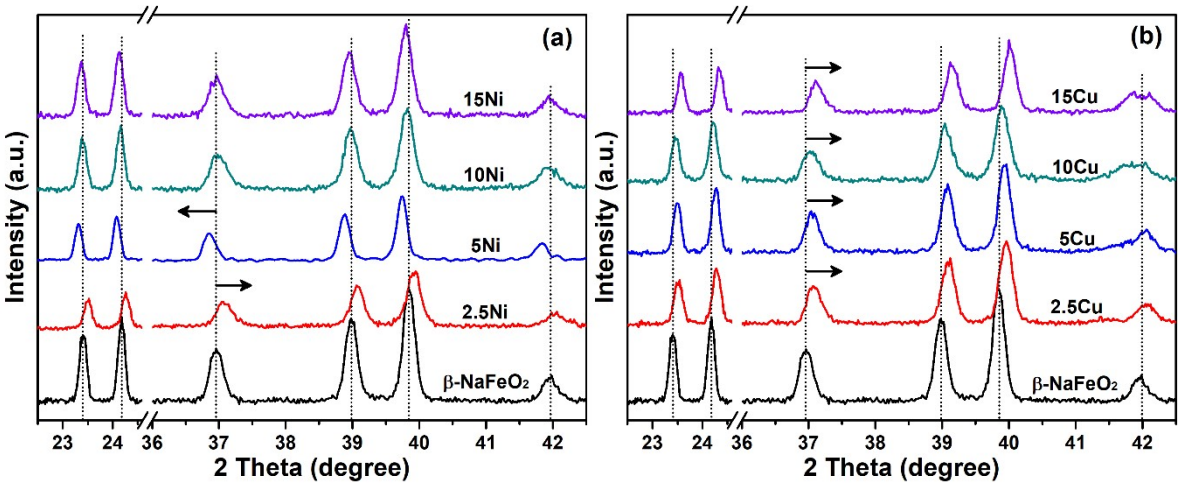

Fig. S1. Amplification of the XRD patterns, showing the most intense peaks coming from the β-$NaFeO_2$ phase for each sample series: (a) *X*Ni-$NaFeO_2$ and (b) *X*Cu-$NaFeO_2$.

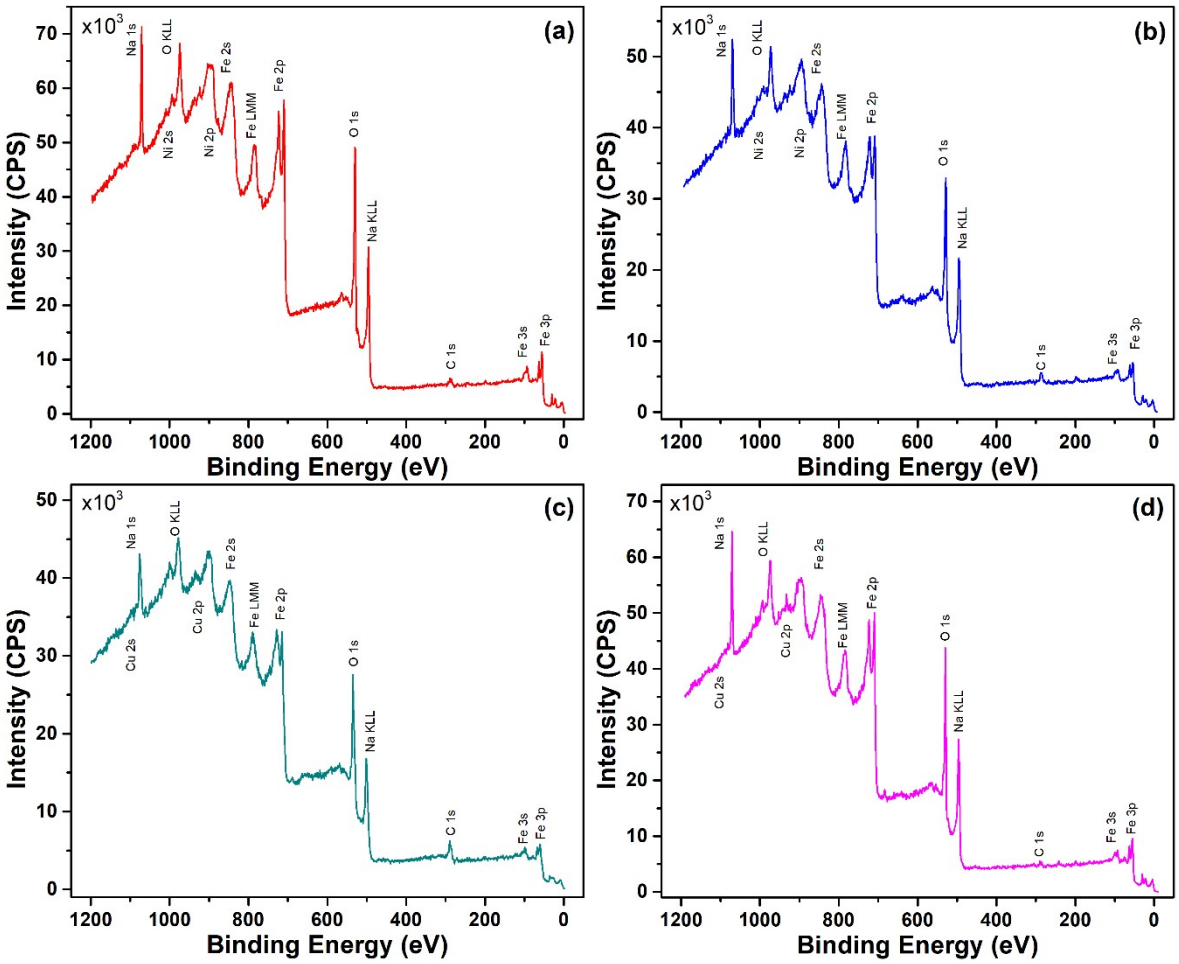

Fig. S2. XPS survey spectra of: (a) 2.5Ni-$NaFeO_2$, (b) 5Ni-$NaFeO_2$, (c) 2.5Cu-$NaFeO_2$ and (b) 5Cu-$NaFeO_2$ samples.

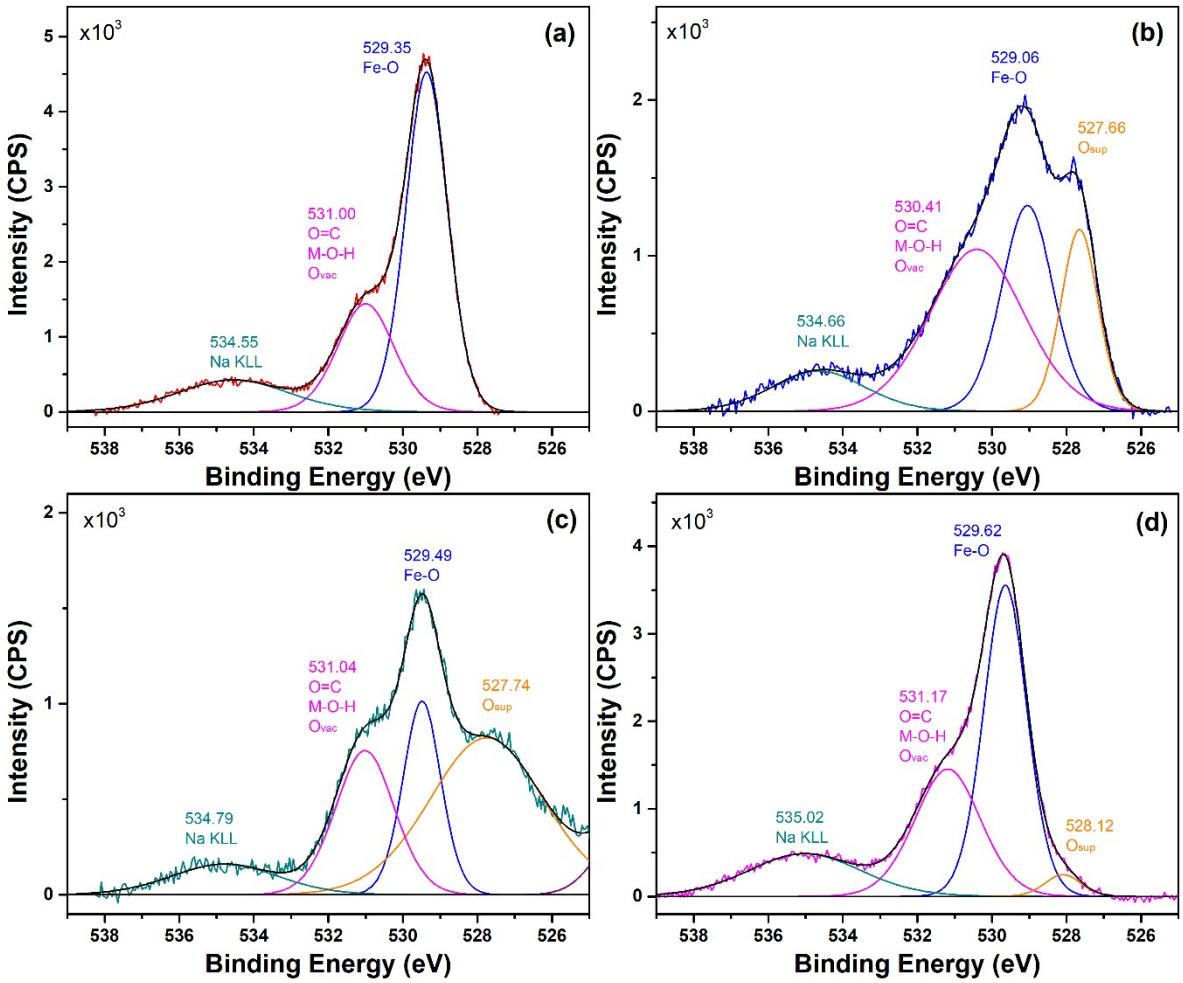

Fig. S3. High resolution XPS spectra of the O 1s edge: (a) 2.5Ni-$NaFeO_2$, (b) 5Ni-$NaFeO_2$, (c) 2.5Cu-$NaFeO_2$ and (d) 5Cu-$NaFeO_2$ samples.

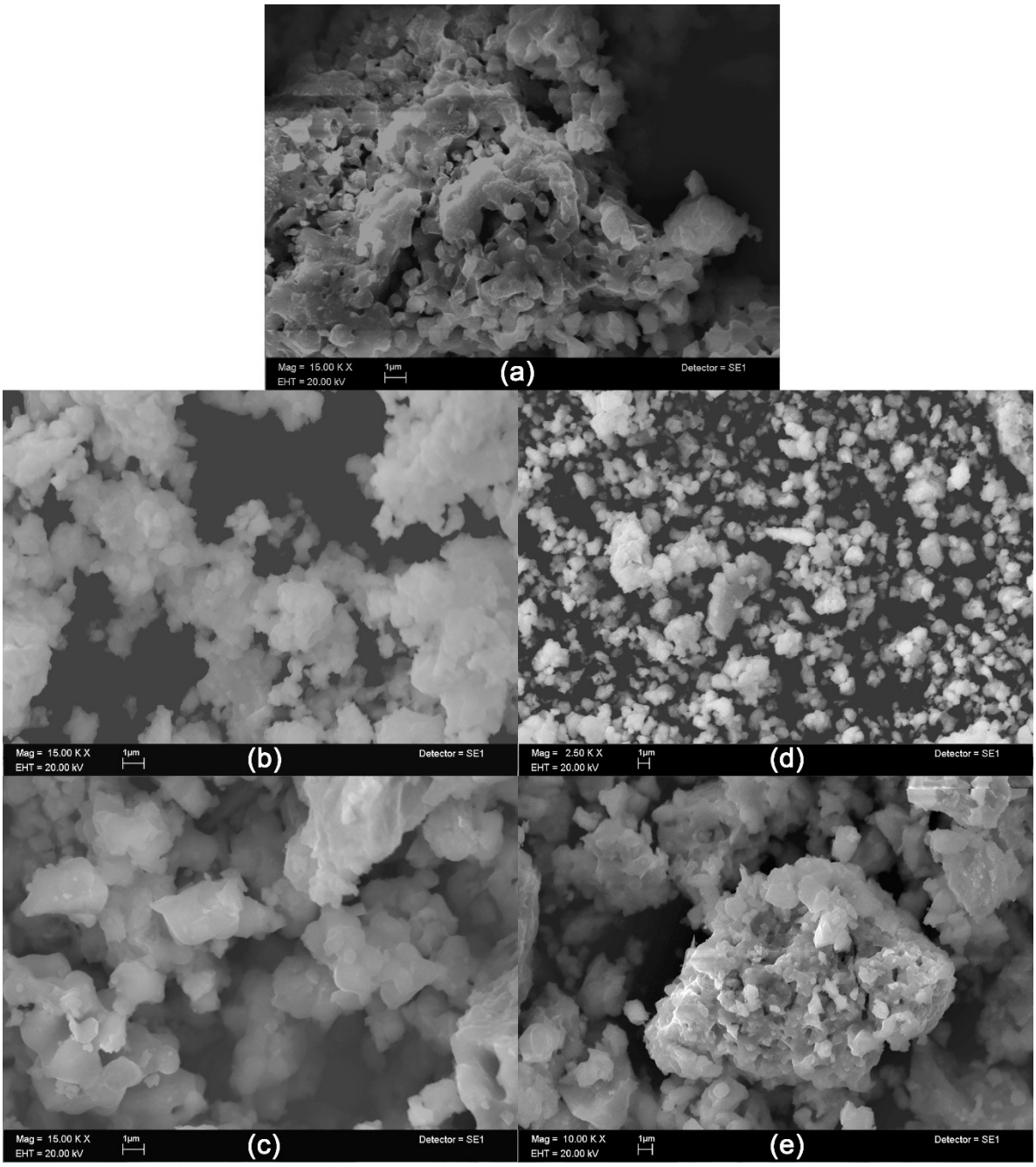

Fig. S4. Representative secondary electron images of selected *X*M-$NaFeO_2$ doped ferrites: (a) Pristine β-$NaFeO_2$, (b) 5Ni-$NaFeO_2$, (c) 5Cu-$NaFeO_2$, (d) 2.5Ni-$NaFeO_2$ and (e) 2.5Cu-$NaFeO_2$.

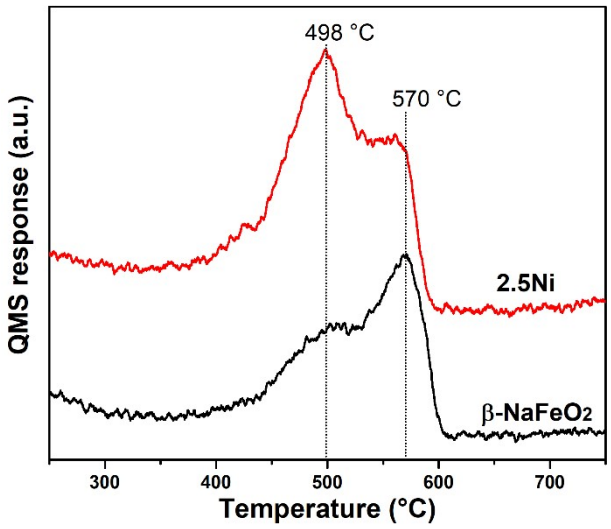

Fig. S5. CO_2-TPD desorption profiles for the pristine β-$NaFeO_2$ and 2.5Ni-$NaFeO_2$ samples thermally treated from 200 to 800 °C in a N_2 flow.

S.2 DFT calculations

Table S1. Cell parameter values (Å) of the fully relaxed orthorhombic β-$NaFeO_2$ structure. The lattice parameters are labeled as **a**, **b**, and **c**.

Axis	Cell parameter values (Å)		
	Calculated – DFT+U	**Experimental – Rietveld**	**Reference** [75]
a	5.779	5.668	5.682
b	5.419	5.384	5.425
c	7.155	7.146	7.235

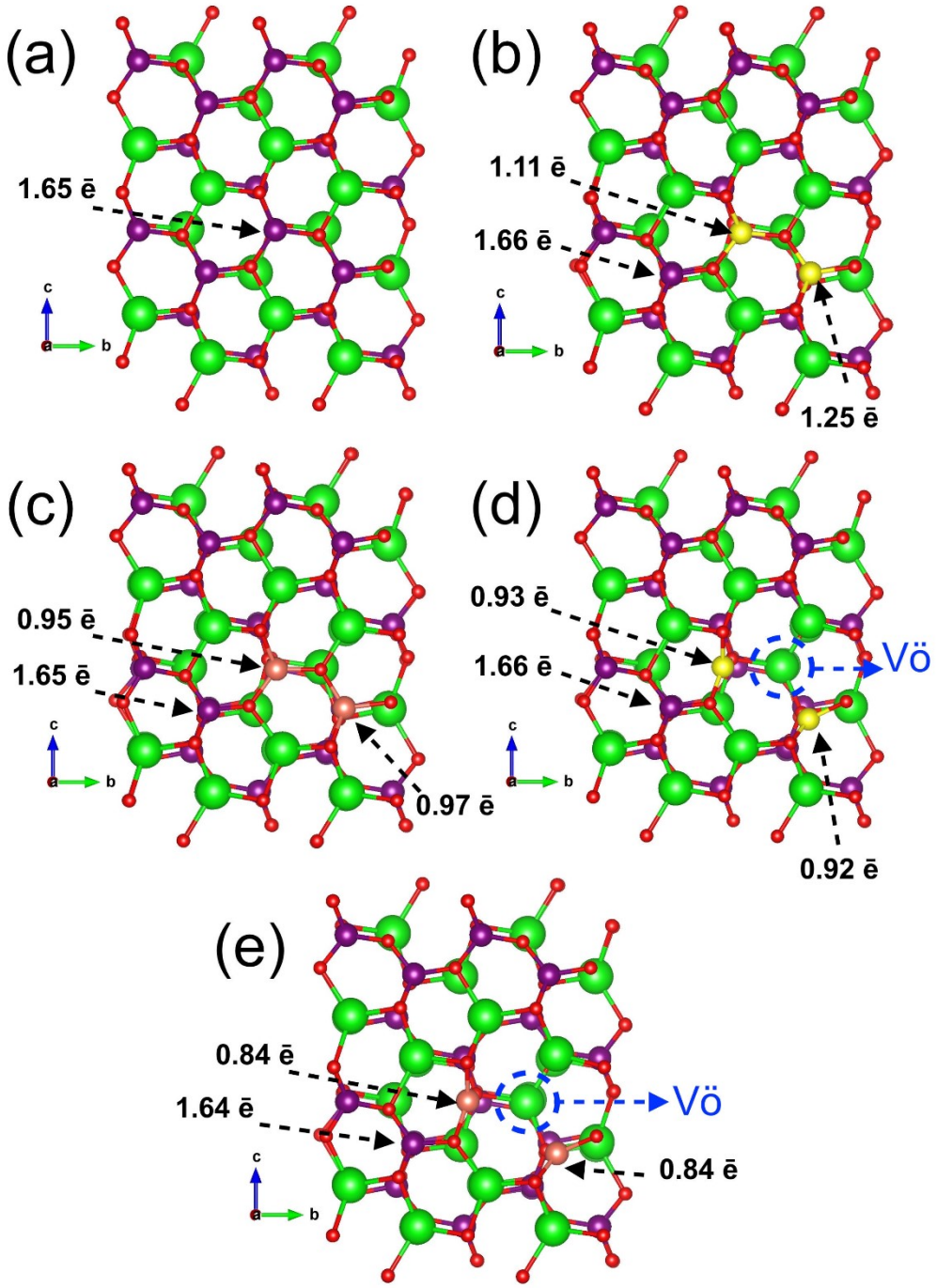

Fig. S6. Relaxed atomic geometries for: (a) pristine β-$NaFeO_2$, (b) Ni-$NaFeO_2$, (c) Cu-$NaFeO_2$, (d) Ni-$NaFeO_2$-Vö, and (e) Cu-$NaFeO_2$-Vö structures. Colour code: Na (Green), O (Red), Fe (Purple), Ni (Yellow), and Cu (Bronze). The site of oxygen vacancy is denoted by the blue dotted circle. The text and black arrows indicate the Bader charge population computed by DFT+U method.

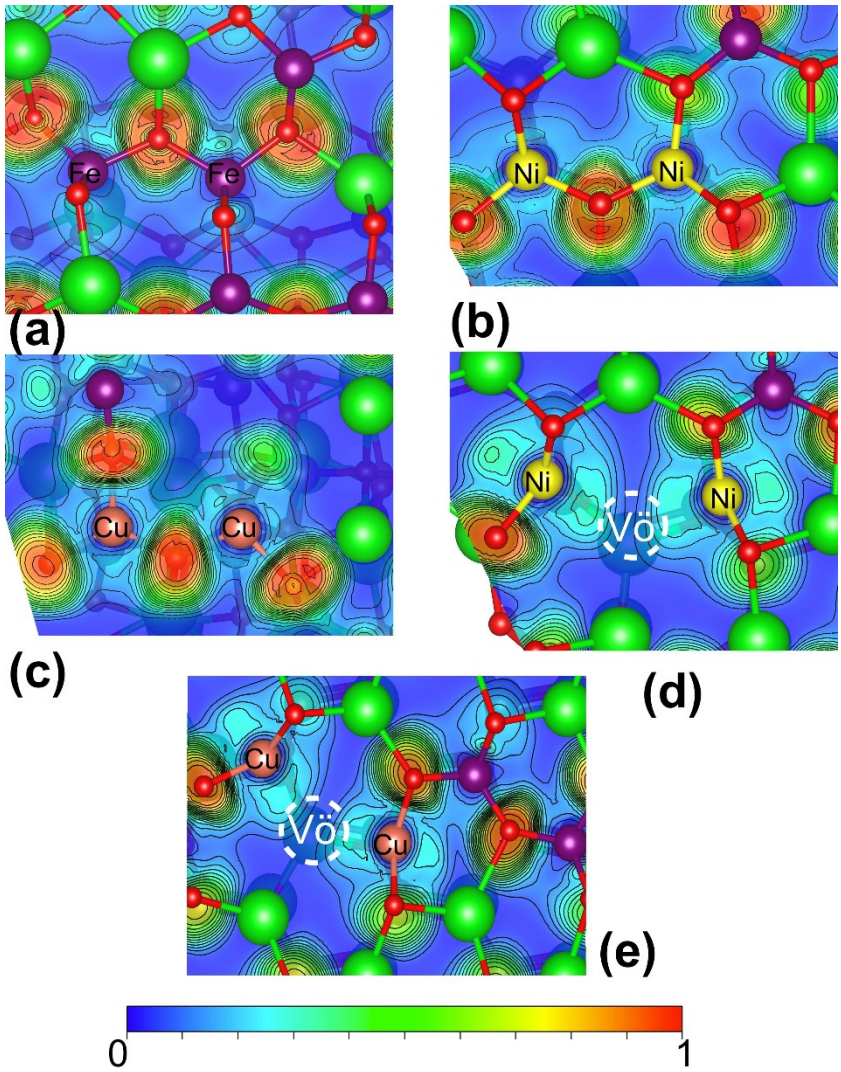

Fig. S7. 2D slice of the electronic localization function (ELF) for: (a) pristine β-$NaFeO_2$, (b) Ni-$NaFeO_2$, (c) Cu-$NaFeO_2$, (d) Ni-$NaFeO_2$-Vö, and (e) Cu-$NaFeO_2$-Vö structures. Colour code: Na (Green), O (Red), Fe (Purple), Ni (Yellow), and Cu (Bronze). The oxygen vacancy site is denoted by the blue dotted circle.

Table S2. Geometrical parameters (Å) of the fully relaxed pristine and M-doped ferrites. Values were calculated at the spin-polarized GGA-PBE level of theory.

Bond type	Bond length (Å)				
	β-$NaFeO_2$	**Ni-$NaFeO_2$**	**Cu-$NaFeO_2$**	**Ni-$NaFeO_2$-Vö**	**Cu-$NaFeO_2$-Vö**
Na–O	2.473	2.437	2.470	2.428	2.297
Fe–O	1.840	1.836	1.838	1.838	1.814
Na–Fe	3.283	3.494	3.285	3.294	3.512
M–O[a]	n/a	1.929	2.001	1.865	1.922

[a]M is associated with Ni or Cu

Table S3. Theoretical (Theo.) and experimental (Exp.) band gap energy (E_{gap}) values, band gap difference (ΔE_{gap}), relative error (E_{error}), and magnetization moment (μ_B) of the pristine and M-doped ferrites, calculated at the spin-polarized GGA-PBE level of theory.

System	E_{gap} (eV)		ΔE_{gap} (eV)	E_{error} (%)	Magnetization moment (μ_B)
	Theo.	*Exp.*			
β-$NaFeO_2$	1.87	1.80	0.07	3.88	n/a
Cu-$NaFeO_2$	1.90	1.76-1.78	0.13	7.34	-0.57
Ni-$NaFeO_2$	1.97	1.82-1.81	0.16	8.83	-0.13
Cu-$NaFeO_2$-Vö	1.76	1.76-1.78	0.01	0.56	-0.48
Ni-$NaFeO_2$-Vö	1.85	1.82-1.81	0.04	2.20	-1.53

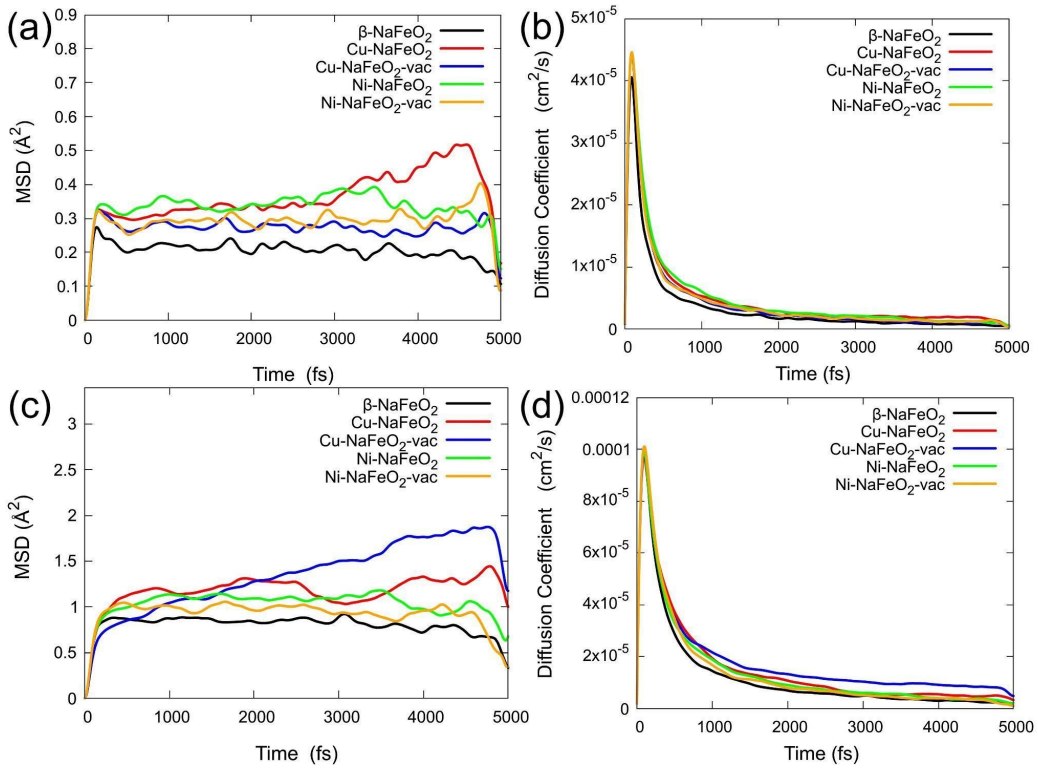

Fig. S8. Mean square displacements (MSD), and diffusion coefficient of Na in sodium ferrite systems at (a-b) a temperature of T = 200 °C, and (c-d) T= 800 °C. The Na diffusion coefficient was obtained according to $D_{Na} = \frac{1}{6t}\left[\sum_i \left|\Delta \vec{r}_i(t)\right|^2\right]$

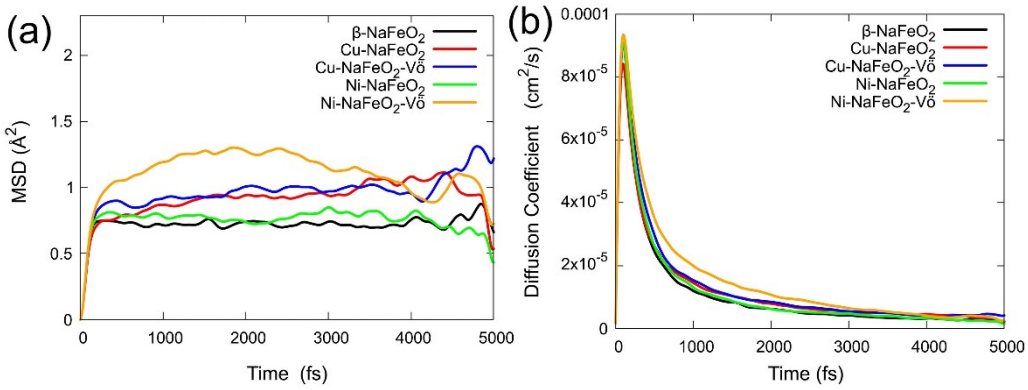

Fig. S9. (a) Mean square displacements (MSD), and (b) Na diffusion coefficient in the sodium ferrite systems at T = 700 °C.

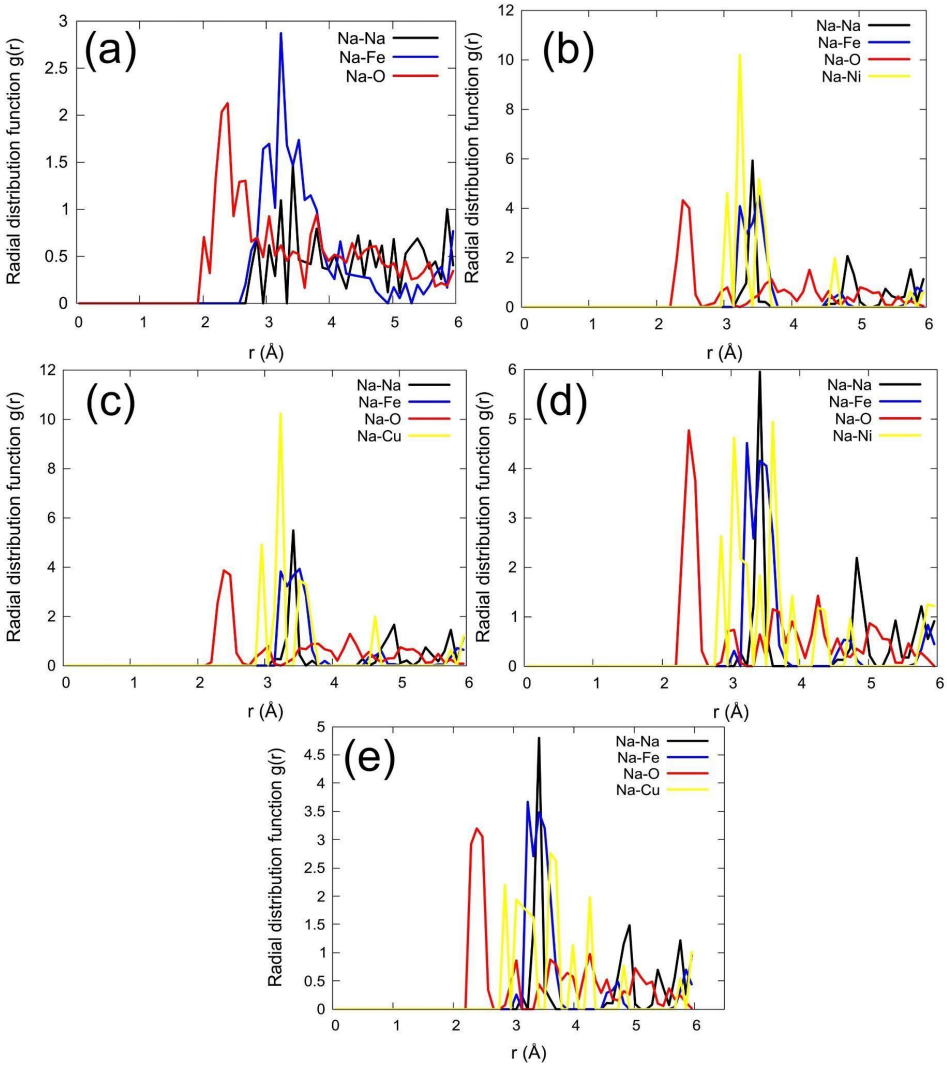

Fig. S10. Radial distribution functions (RDF) at a temperature of T = 200 °C obtained with the AIMD simulations: (a) pristine β-$NaFeO_2$, (b) Ni-$NaFeO_2$, (c) Cu-$NaFeO_2$, (d) Ni-$NaFeO_2$-Vö, and (e) Cu-$NaFeO_2$-Vö structures.

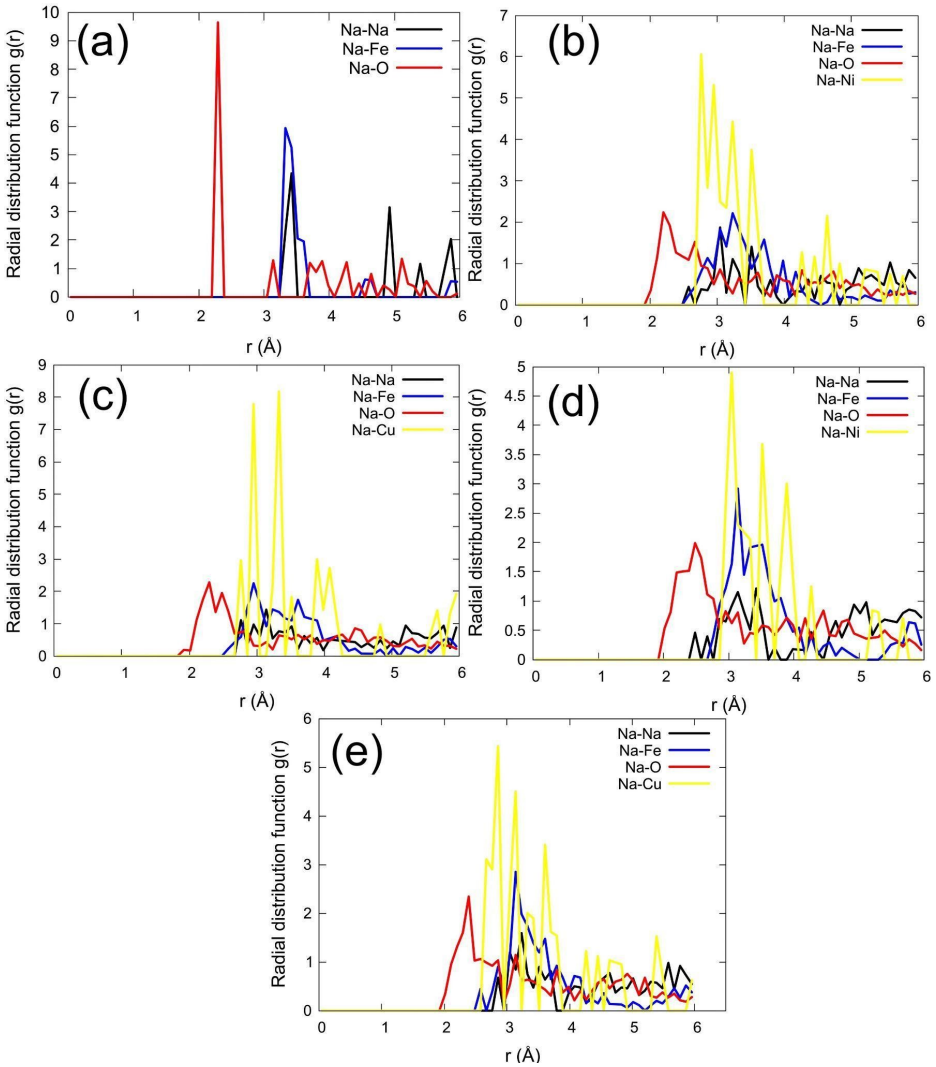

Fig. S11. Radial distribution functions (RDF) at a temperature of T = 800 °C obtained with the AIMD simulations: (a) pristine β-$NaFeO_2$, (b) Ni-$NaFeO_2$, (c) Cu-$NaFeO_2$, (d) Ni-$NaFeO_2$-Vö, and (e) Cu-$NaFeO_2$-Vö structures.

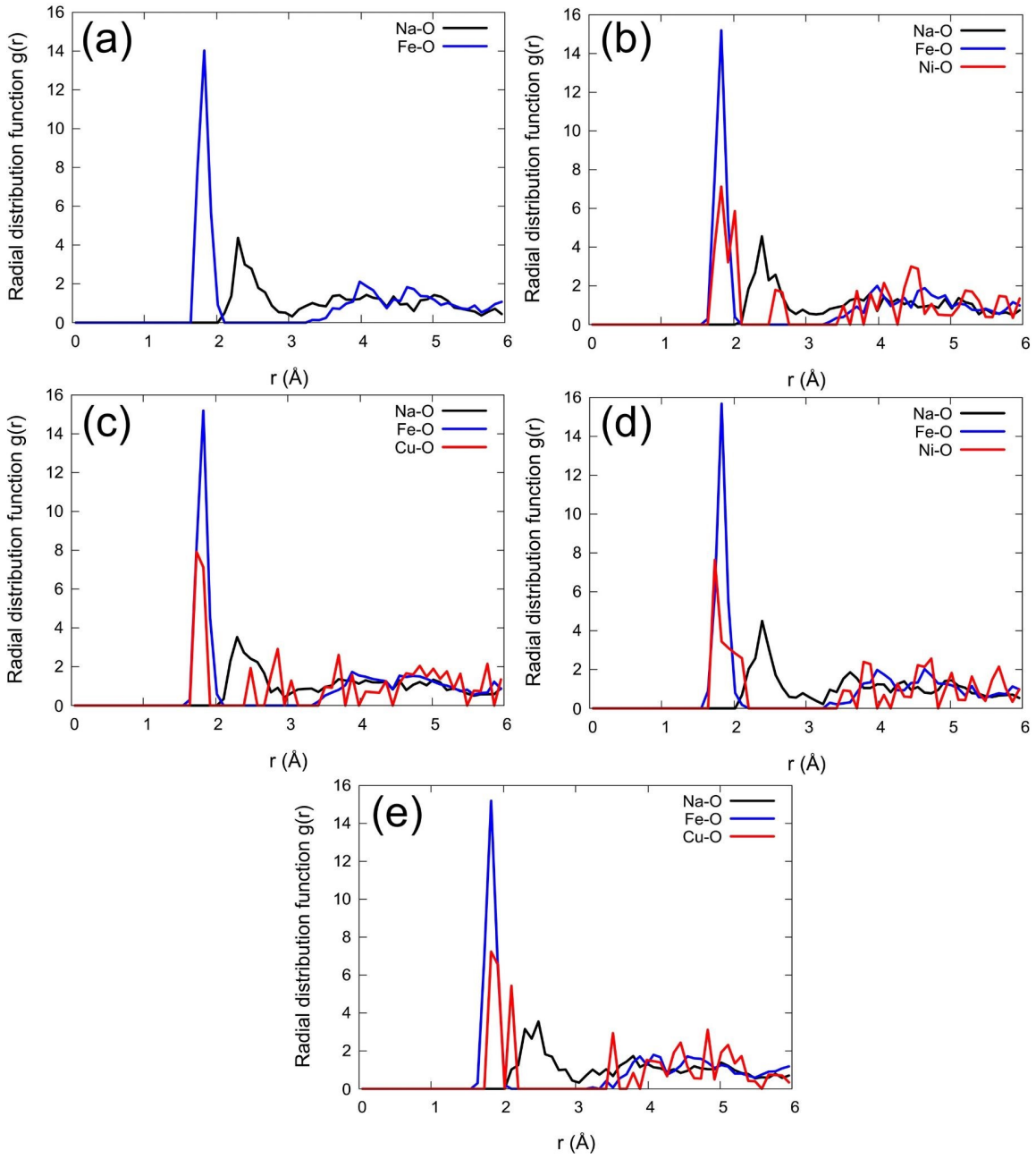

Fig. S12. Radial distribution functions (RDF) for oxygen interaction at a temperature of T = 200 °C obtained with the AIMD simulations: (a) pristine β-$NaFeO_2$, (b) Ni-$NaFeO_2$, (c) Cu-$NaFeO_2$, (d) Ni-$NaFeO_2$-Vö, and (e) Cu-$NaFeO_2$-Vö structures.

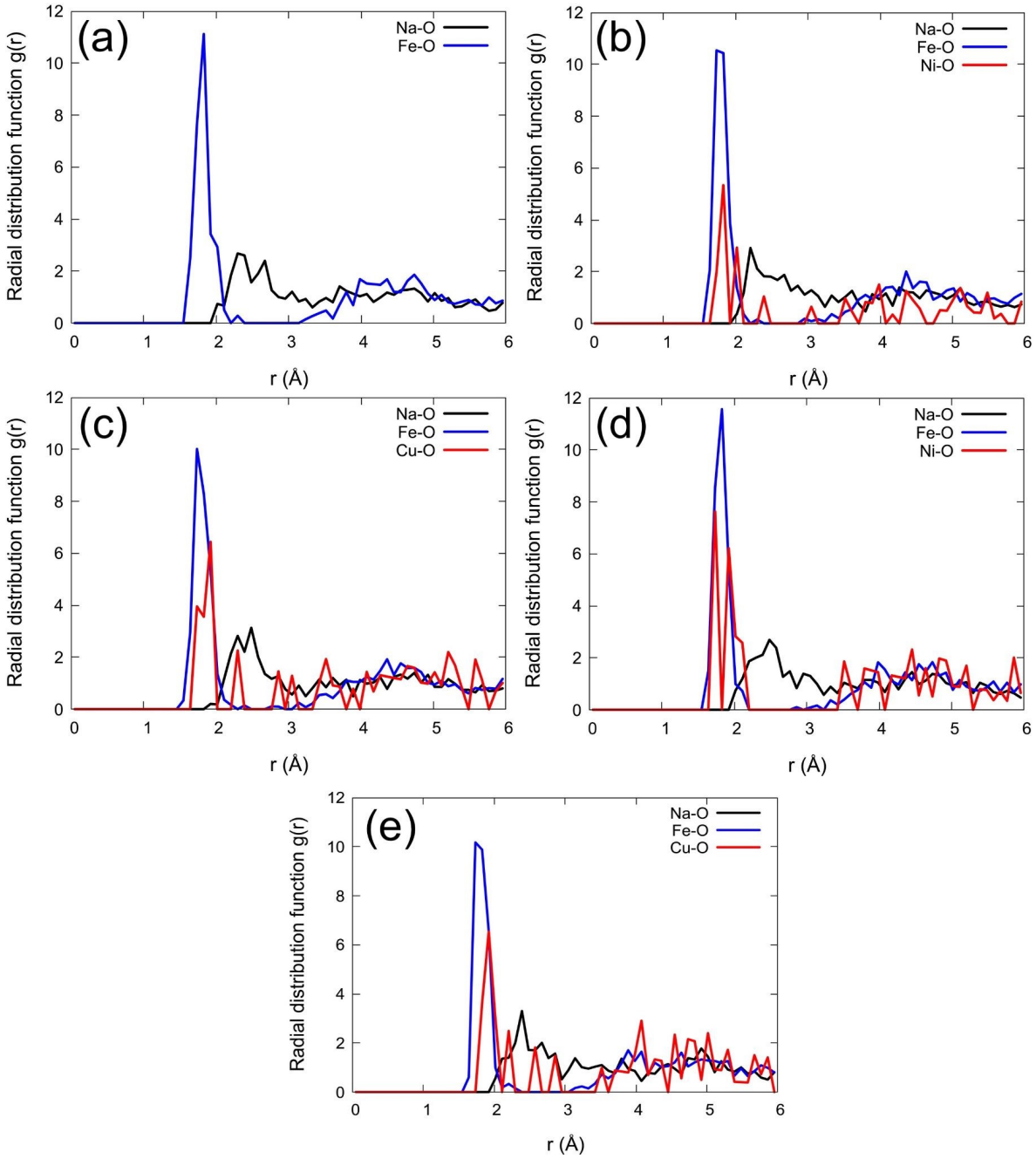

Fig. S13. Radial distribution functions (RDF) for oxygen interaction at a temperature of T = 800 °C obtained with the AIMD simulations: (a) pristine β-$NaFeO_2$, (b) Ni-$NaFeO_2$, (c) Cu-$NaFeO_2$, (d) Ni-$NaFeO_2$-Vö, and (e) Cu-$NaFeO_2$-Vö structures.